

Radiocarbon Dating

B. A. Buchholz

May 29, 2012

Wiley Encyclopedia of Forensic Science

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

FSA 608

Radiocarbon Dating

Bruce A. Buchholz, Ph.D. Center for Accelerator Mass Spectrometry Lawrence Livermore National Laboratory Livermore, CA 94551 USA E-mail: bbuchholz@llnl.gov

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Abstract:

Radiocarbon dating can be used to determine the age of objects that contain components

that were once alive. In the case of human remains, a radiocarbon date can distinguish

between a crime scene and an archeological site. Documents, museum artifacts and art

objects can be dated to determine if their age is correct for the historical context. A

radiocarbon date does not confirm authenticity, but it can help identify a forgery.

Keywords: Carbon-14, C-14, radiocarbon dating, isotope dating

INTRODUCTION

Radiocarbon dating is traditionally considered an archeological tool rather than a forensic one. Radiocarbon or carbon-14 (¹⁴C) is produced naturally in the atmosphere by cosmic ray interactions with nitrogen. Single carbon atoms in the atmosphere are chemically reactive and are quickly oxidized to carbon dioxide CO₂. The CO₂ from the atmosphere is incorporated into plants and works its way up the food chain to label every living thing with ¹⁴C. The natural atmospheric concentration of natural ¹⁴C with respect to all carbon has remained relatively stable at about 1.2 parts per trillion over the past several thousand years with the exception of the radiocarbon bomb-pulse since 1955 (See Carbon-14 Bomb-Pulse Dating). With a radioactive half-life of 5730 years, the radioactive decay of ¹⁴C is minimal within the time periods of interest in most medical forensic cases and applicable for samples over 300 years of age. Willard Libby was awarded the Nobel Prize in Chemistry in 1960 for the development of radiocarbon dating [1].

BASICS OF RADIOCARBON DATING

Radiocarbon dating relates the ¹⁴C /C ratio in a sample to an extensive historical record to determine the age of a sample. Radiocarbon is produced naturally in the upper atmosphere by reactions of nitrogen with neutrons produced by cosmic ray interactions in the atmosphere. The natural production of ¹⁴C varies slightly over time due to fluctuations in the Earth's magnetic field and variations in the cosmic ray flux striking the earth. Newly produced ¹⁴C is quickly oxidized to carbon dioxide (¹⁴CO₂) and mixes in the

atmosphere. Everything alive is labeled by ¹⁴C. Plants incorporate CO₂ directly from the atmosphere and animals acquire ¹⁴C by eating plants or other animals, and the label moves up the entire food chain. All living things continue to renew their carbon inventories throughout their lives. The rate of radioactive decay of ¹⁴C is relatively slow and predictable, so the concentration of ¹⁴C changes slowly and reliably over time once a biological material dies and stops incorporating new carbon into its structure. The decrease in ¹⁴C/C concentration from the contemporary value is used to determine the age of the sample. Extensive geological and archeological records are used to account for the variations in atmospheric ¹⁴C concentration over the chronological range of radiocarbon dating (300-50,000 years before present) [2-4]. Any sample greater than 50,000 years old has too little ¹⁴C to measure accurately. There is some debate over the accuracy of the ¹⁴C calibration between 40,000 and 50,000 years before present, but it is hard to conceive of a forensic sample of this age. Fossil carbon, either coal or petroleum, is older than 60,000 years and free of ¹⁴C.

MEASUREMENT OF RADIOCARBON SAMPLES

Today most ¹⁴C dating analyses are conducted using accelerator mass spectrometry (AMS), although some labs still use decay counting. AMS is much faster and generally more precise than decay counting since it measures differences in carbon atom mass and is not constrained to wait for atomic decay. AMS can also use smaller samples than decay counting, an important issue when analyzing evidence or artifacts. There are about 100 AMS facilities world-wide.

Sample preparation and measurement details vary among AMS facilities, depending on the type of sample to be analyzed and the design of spectrometer. Routine radiocarbon analyses using accelerator mass spectrometry (AMS) are performed on samples containing 0.3-1.0 milligram carbon. Samples as small as 20 µg carbon can be analyzed at some labs, but measurement uncertainties are larger. Nearly all AMS facilities that perform high precision dating follow these general procedures to minimize contamination from outside sources of carbon and reduce measurement backgrounds. Samples are dried completely and then combusted with excess oxygen to produce CO₂. The CO₂ is purified to remove water vapor, nitrogen, oxides of nitrogen, and oxides of sulphur. It is then reduced to graphite or elemental carbon on metal catalyst, often cobalt or iron powder.

Primary standards, secondary standards, and backgrounds are similarly processed to produce graphite, which is form of carbon analyzed by the majority of AMS systems. Graphite is the preferred form of carbon because it can be made easily at high purity, produces intense negative ion currents, and can be prepared at satellite labs and shipped to AMS facilities for analysis. A handful of gas accepting ion sources that take direct feed of CO₂ exist, but they are not yet typically used for high precision dating. It is important to have consistent sample source material (e.g., all graphitic carbon or all CO₂) because different molecules ionize with different efficiencies. Methods for producing graphite for elevated biological tracing experiments are generally unsuitable for radiocarbon dating due to larger sample-to-sample variation and higher background [5,6].

The precision of radiocarbon dating depends on the ability to measure the 14 C concentration in a sample and the shape of the calibration curve. It is relatively easy to achieve 0.5-0.8% precision when analyzing relatively young full-sized samples. This measurement precision translates to a chronological uncertainty of \pm 30-60 years in most samples less than 10,000 years old. Samples more than 25,000 years old can still be measured to 1% precision, but uncertainty propagation from backgrounds and the calibration curve typically yields uncertainties greater than \pm 100 years. The conventions for reporting radiocarbon dates are described by Stuiver and Polach [7].

SAMPLES AMENABLE TO DATING

Anything that was alive in the past is amenable to radiocarbon dating. Charcoal, wood, straw, hair, cloth, and bones are often dated in archeological sites. Historical documents and works of art are also routinely dated to confirm that the paper or canvas is of the appropriate age for the object.

Bone

Bone is the preferred sample matrix for dating human remains. Bone's ability to resist decay while containing a relatively high concentration of carbon makes it a desirable material for traditional dating. The carbon in collagen does turnover slowly while a person is alive, so the ¹⁴C content is really a lifetime average rather than a snapshot in time. Traditional bone dating uses a collagen extraction to avoid potential complications

with mineral exchange of carbonates in bone in the environment. Collagen is a protein and is not affected by environmental carbonate exchange like the mineral component of bone.

Specific procedures for collagen extraction vary slightly among labs. In general, the mineral component of bone is dissolved in acid to free the collagen into solution. A variety of washing, rinsing and filtering techniques are then applied to purify the collagen. Once purified, it can be combusted like any organic sample.

If human remains are found without any other evidence, radiocarbon analysis of bone collagen or hair can determine whether authorities have a crime scene (see Carbon-14 Bomb Pulse Dating) or an archeological site. If the ¹⁴C content of the collagen is elevated above the level in 1950, the person died sometime after 1955. The decrease in ¹⁴C concentration due to decay can be measured over a 100 years, but the small differences in natural production between 1650-1955 and the decay combine to make it very difficult to separate samples chronologically over this time. Collagen from before 1650 can be clearly distinguished.

In the United States a ¹⁴C date can determine ownership of remains or precipitate a court battle over ownership, such as the case of Kennewick Man [8-11]. The Native American Graves Protection and Repatriation Act (NAGPRA) requires institutions that receive U.S. federal funding to return of human remains and sacred artifacts to ethnic descendents when they are available.

Documents and art objects

Radiocarbon dating of documents and art objects is routinely done by museums to confirm the items age is consistent with its provenance. This approach only confirms paper, cloth, wood or canvas is the appropriate age, it does not confirm authenticity. A radiocarbon analysis that contains recent bomb pulse carbon identifies a forgery of an older item.

REFERENCES

- Libby WF, Anderson EC, Arnold JR. Age determination by radiocarbon content world-wide assay of natural radiocarbon. Science 1949 109: 227-228.
- Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Bertrand CJH, Blackwell PG, Buck CE, Burr GS, Cutler KB, Damon PE, Edwards RL, Fairbanks RG, Friedrich M, Guilderson TP, Hogg AG, Hughen KA, Kromer B, McCormac G, Manning S, Ramsey CB, Reimer RW, Remmele S, Southon JR, Stuiver M, Talamo S, Taylor FW, van der Plicht J, Weyhenmeyer CE. IntCal04 terrestrial radiocarbon age calibration, 0-26 cal kyr BP. Radiocarbon 2004 46: 1029-1058.
- 3. Reimer PJ, Baillie MGL, McCormac G, Reimer RW, Bard E, Beck JW, Blackwell PG, Buck CE, Burr GS, Edwards RL, Friedrich M, Guilderson TP, Manning S, Guilderson TP, Southon JR, Hogg AG, Stuiver M, Hughen KA, van der Plicht J,

Kromer B, van der Plicht J, Manning S, Weyhenmeyer CE. Comment on "Radiocarbon calibration curve spanning 0 to 50,000 years BP based on paired Th-230/U-234/U-238 and C-14 dates on pristine corals" by R.G. Fairbanks et al. (Quaternary Science Reviews 24 (2005) 1781-1796) and "Extending the radiocarbon calibration beyond 26,000 years before present using fossil corals" by T.-C. Chin et al. (Quaternary Science Reviews 24 (2005) 1797-1808). Quaternary Science Reviews 2006 25: 855-862.

- 4. Reimer PJ, Baillie MGL, Bard E, Bayliss A, Beck JW, Blakwell PG, Bronk Ramsey C, Buck CE, Burr GS, Edwards RL, Friedrich M, Grootes PM, Guilderson TP, Hajdas I, Heaton TJ, Hogg AG, Hughen KA, Kaiser KF, Kromer B, McCormac FG, Manning SW, Reimer RW, Richards DA, Southon JR, Talamo S, Turney CSM, vander Plicht J, Weyhenmeyer CE. IntCal09 and Marine09 Radiocarbon Age Calibration Curves, 0-50,000 Years cal BP. Radiocarbon 2009 51: 1111-1150.
- Vogel JS. Rapid production of graphite without contamination for biomedical AMS.
 Radiocarbon 1992 34: 344-350.
- 6. Ognibene TJ, Bench G, Vogel JS, Peaslee GF, Murov S. A high-throughput method for the conversion of CO₂ obtained from biochemical samples to graphite in septasealed vials for quantification of C-14 via accelerator mass spectrometry. Analytical Chemistry 2003 75: 2192-2196.

- 7. Stuiver, M. and Polach, H.A. Discussion: reporting of ¹⁴C data, *Radiocarbon* 1977 19: 355-363.
- 8. Chatters JC. The recovery and first analysis of an Early Holocene human skeleton from Kennewick, Washington. American Antiquity 2000 65: 291-316.
- Bruning SB. Complex legal legacies: The Native American Graves Protection and Repatriation Act, scientific study, and Kennewick Man. American Antiquity 2006 71: 501-521.
- 10. Huxley AK, Finnegan M. Human remains sold to the highest bidder! A snapshot of the buying and selling of human skeletal remains on eBay^(R), an Internet auction site.

 Journal of Forensic Sciences 2004 49: 17-20.
- 11. Musselman J. Ninth Circuit limits NAGPRA to remains linked with presently existing tribes. Ecology Law Quarterly 2005 32: 707-713.